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Electronic and Ionic Transport in Polymers

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Dennis S. Marynick, Timothy D. Shaffer

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A comparative electrochemical charge transport and morphological study of poly(3-methylthiophene) has shown that the redox switching speed of the polymer is affected by the growth morphology which in turn is affected by the electrolyte. The anodic deactivation of polythiophenes has been examined using voltammetry, coulometry, FT-IR spectroscopy and chemical analyses. Molecular orbital calculations have uncovered steric interactions in polyisothianaphthene and polyisonaphthiophene which causes them to be nonplanar. A series of liquid crystalline polyazomethine ethers with two different highly conjugated mesogenic units and flexible alkyl spacers have been prepared and studied with  $^{13}\text{C}$  CP/MAS NMR spectroscopy and by comparison with model compounds. Anomalous amino end groups, which give rise to distorted thermal behavior, could be end capped with benzaldehyde. These compounds were found to exhibit nematic mesomorphism. For the first time a transition metal [Ni(II) and Cu(II)] has been used to control the mesomorphic character of a liquid crystal. Thus, chelates using N, N'-bis(5-alkoxysalicyl-idene)ethylene diamine (Salen) show smectic mesomorphism whose transition temperatures could be controlled by changing the transition metal or by varying the length of the alkoxy unit.

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## Technical Report

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## Description of Progress

A comparative electrochemical charge transport and morphological study has been carried out on poly(3-methylthiophene) in a variety of electrolytes. The polymer growth morphology is highly affected by the electrolyte used which directly influences the redox switching speeds of the polymer. Smooth film formation, as opposed to fractal-like deposits, is required for fast response. In this study, tetrabutylammonium tetrafluoroborate was found to produce the highest quality material.

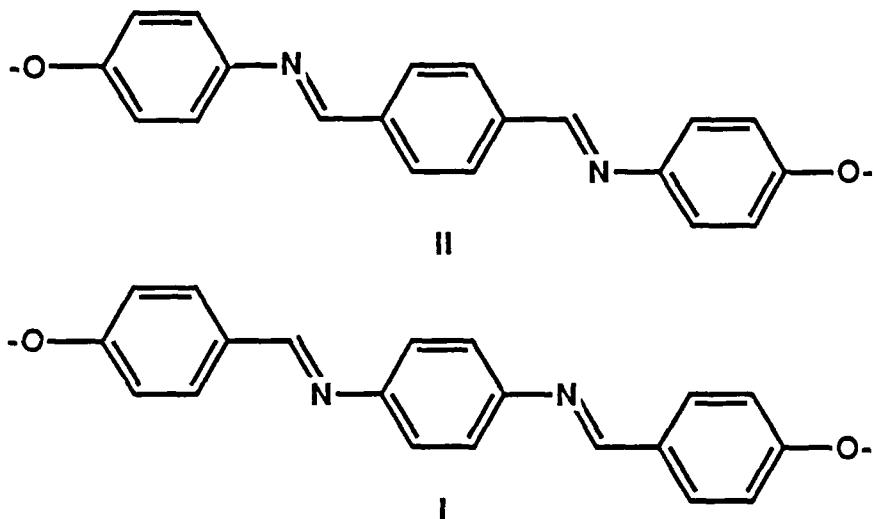
In order to produce high temperature electronically active composites, an agreement has been reached with BASF Structural Materials Inc. and Narmco Materials Inc. to use their 5250-2 bismaleimide resin system. Electroactive polymer composites, prepared in our laboratories, will be investigated by the Materials Response Group at General Dynamics (Fort Worth). In a second route to high temperature stability in conductive polymers, a modified Kevlar polyelectrolyte has been developed and shown to be useful in the electrosynthesis of polypyrrole films. Initial films have electrical conductivities of  $10^{-3} \Omega^{-1} \text{ cm}^{-1}$ .

The electrochemical behavior of ethylmercapto-substituted polythiophenes has continued to be studied using a combination of voltammetry, coulometry, FT-IR spectroscopy and chemical analyses. The anodic deactivation of these polymers as well as polythiophenes in general has been studied in detail for the first time. A manuscript detailing these results has been submitted to the *Journal of Electroanalytical Chemistry*.

A short communication on the strategy of fluorescence modulation using redox switching of polypyrrole has been accepted for publication in the *Journal of the Chemical Society, Chemical Communications*.

Molecular orbital calculations have shown that polyisothianaphthene and polyisonaphthiophene are non-planar polymers, due to steric interactions between the sulfur and hydrogens from an adjacent monomeric unit. This result has important implications for the design of conducting polymers.

We have completed the structural and property analyses of a series of potentially conducting liquid crystalline polyazomethine ethers containing structure I or II as the mesogenic core and flexible alkyl spacers. The results of this work have been submitted to *Macromolecules* for publication.



The structural analysis was done using CP/MAS  $^{13}\text{C}$  NMR spectroscopy. NMR assignments were made by comparing with the CP/MAS and solution  $^{13}\text{C}$  NMR resonances of model compounds (methoxy substituted structures I and II). These experiments along with FT-IR spectroscopy helped confirm the presence of *only* amine termination in the prepared polymers. The polymers so terminated exhibited distorted thermal behavior attributed to amine H-bonding and thermally induced molecular weight redistribution. Reproducible thermal behavior could be obtained by removing these chain ends with benzaldehyde end-capping.

The mesomorphic properties of the polymer series were compared to each other and to the model compounds. In both the polymeric and model compounds, structure I (with two nitrogens bonded to the same phenyl ring) gave rise to slightly higher transition temperatures ( $T_m$ ,  $T_i$ ) than its configurational analog. The magnitudes of these differences, however, are much smaller than variations found by changing the length of the alkyl spacer. Methoxy derivatives of structures I and II were found to exhibit a similar thermal relationship. All of these materials only exhibit nematic mesomorphism. Consequently, the two structures can be interchanged without drastically altering mesomorphic properties. Since we now have an understanding of the structure-property relationships in these systems, we have begun to study any potential electroactivity in these polymers. Furthermore, we have expanded this project to polyazomethine ethers with longer conjugation lengths and oligo(oxyethylene)s as flexible spacers.

We have completed a pioneering model study of liquid crystalline transition metal complexes of *N,N'*-bis(5-alkoxysalicylidene)ethylene diamine (Salen). The results of this work has been submitted to *Molecular Crystals and Liquid Crystals* for publication.

For the first time, a transition metal has been used to control the mesomorphic character of a liquid crystal. Chelates prepared from Ni(II) and Cu(II) exhibited smectic mesomorphism whose transition temperatures were controlled by varying the length of the alkoxy unit. A more significant degree of control was observed by changing the transition metal. Decomposition was dominant in the thermal characteristics of Salen-Cu(II) alkyl

ethers. The Ni(II) analogs are significantly more thermally stable. In all complexes, except one, only smectic mesomorphism was observed.

The differences in the thermal characteristics between the Cu(II) and Ni(II) complexes is attributed to the different electronic structures of the chelated metals. Only in Cu(II) is a Jahn-Teller distortion permitting strong intermolecular interactions in bulk. Ni(II) complexes need not distort for square planar coordination and do not participate in axial ligation. Here only the molecular structure is important in generating liquid crystalline behavior.

### Personnel Changes

Dr. Kamlesh A. Sheth joined the group on May 1, 1988, as a postdoctoral associate.

Ms. L. Phan has completed her M.S. in Chemistry. Her thesis topic in part focused on the fluorescence modulation technique.

Mr. Yeunghaw Ho has joined the project as a graduate student.

### Publications

#### Papers Published

Panchalingam, V. and Reynolds, J.R., "Structural Analysis of the Alternating Copolymer Poly(chloroacrylonitrile-*alt*-cyclohexadiene)", *Macromolecules* **21**, 960 (1988).

Martinez, M.; Reynolds, J.R.; Basak, S.; Black, D.; Marynick, D.S. and Pomerantz, M., "Electrochemical Synthesis and Optical Analysis of Poly[(2,2'-dithienyl)-5,5'-diylvinylene]", *J. Polym. Sci. Phys. Ed.* **26**, 911 (1988).

Tsai, E.W.; Pajkossy, T.; Rajeshwar, K. and Reynolds, J.R., "Anion Exchange Behavior of Polypyrrole Membranes", *J. Phys. Chem.*, **92**, 3560 (1988).

#### Papers in Press

Reynolds, J.R., "Electrically Conductive Polymers: Processible, Stable and Useful", *Chemtech*, in press.

Reynolds, J.R.; Sundaresan, N.S.; Pomerantz, M.; Basak, S. and Baker, C.K., "Self-Doped Conducting Copolymers: A Charge Transport Study of Poly{pyrrole-co-[3-(pyrrol-1-yl)propanesulfonate]}", *J. Electroanal. Chem.*, in press.

Wang, F. and Reynolds, J.R., "Soluble and Electroactive Nickel Bisdiethiolene Complex Polymers", *Macromolecules*, in press.

Baker, C.K. and Reynolds, J.R., "A Quartz Microbalance Study of the Electrosynthesis of Polypyrrole", *J. Electroanal. Chem.*, in press.

Tsai, E.W., Phan, L. and Rajeshwar, K., "Electrochemical Modulation of Luminescence from an Interfacial Probe During Redox Switching of Polypyrrole", *J. Chem. Soc. Chem. Commun.*, in press.

Reynolds, J.R.; Baker, C.K.; Martinez, M.; Poropatic, P.A.; Sundaresan, N.; Pomerantz, M.; Basak, S.; Marynick, D.S. and Black, D.A., "Structural Control of the Electronic and Ionic Properties of Polyheterocycles", *Proceedings of the Symposium on the Emergence of Conducting Polymers*, 193rd National Meeting of the American Chemical Society, April 1987, in press.

Pomerantz, M.; Cardona, R. and Rooney, P., "The Application of the PMO Method to Aromatic Conducting Polymers", *Macromolecules*, in press.

Shaffer, T.D., "Phase Transfer Catalyzed Polymerization of  $\alpha,\alpha'$ -Dibromoxylene Isomers", *J. Polym. Sci., Polym. Lett. Ed.*, in press.

### **Papers Submitted for Publication**

Mori, E.; Baker, C.K.; Reynolds, J.R. and Rajeshwar, K., "Aqueous Electrochemistry of Tellurium at Glassy Carbon and Gold: A Combined Voltammetry-Oscillating Quartz Crystal Microgravimetry Study", *J. Electroanal. Chem.*, submitted.

Ruiz, J.P.; Reynolds, J.R.; Nayak, K. and Marynick, D.S., "Soluble Ethylmercapto Substituted Polythiophenes", *Macromolecules*, submitted.

Reynolds, J.R.; Baker, C.K.; Jolly, C.A.; Poropatic, P.A. and Ruiz, J.P., "Electrically Conductive Polymers", *Conductive Polymers and Plastics*, Chapman and Hall, submitted.

Tsai, E.W.; Basak, S.; Ruiz, J.P.; Reynolds, J.R. and Rajeshwar, K., "Electrochemistry of Some  $\beta$ -Substituted Polythiophenes. Anodic Oxidation, Electrochromism and Electrochemical Deactivation Behavior", *J. Electroanal. Chem.*, submitted.

Shaffer, T.D. and Shaffer, M.L., "Configurational Isomerism and Structural Characterization of Mesomorphic Aliphatic-Aromatic Polyazomethine Ethers", *Macromolecules*, submitted.

Shaffer, T.D. and Sheth, K.A., "Mesomorphic Transition Metal  $N_2O_2$  Chelates", *Mol. Cryst. Liq. Cryst.*, submitted.

### **Meetings Attended and Papers Presented**

Two principal investigators, John Reynolds and Martin Pomerantz, one postdoctoral fellow and five graduate students attended the International Conference on the Science and Technology of Synthetic Metals in Santa Fe, New Mexico, on June 27-July 1. The following presentations were given:

1. Electroactive and Soluble Polyheterocycles and Transition Metal Complex Polymers. John R. Reynolds, Jose P. Ruiz, Fei Wang, Cynthia A. Jolly, Kasinath Nayak and Dennis S. Marynick.

2. Gravimetric and Electrochemical Analysis of Polyheterocycles Using the Quartz Crystal Microbalance. Charles K. Baker and John R. Reynolds.

3. Soluble and Electroactive Transition Metal Complex Polymers. Cynthia A. Jolly, Fei Wang, Slaheddine Krichene and John R. Reynolds.

4. The Effect of Structural Modification on the Physical and Electronic Properties of Polythiophenes. Jose P. Ruiz, Melinda B. Gieselman, K. Nayak, Dennis S. Marynick and John R. Reynolds.

John Reynolds attended a symposium on conducting polymers at the Middle Atlantic Regional Meeting of the American Chemical Society on May 24-26. He presented a talk entitled "The Effect of Structural Modification on the Physical and Electronic Properties of Polythiophenes".

Two posters were presented at the Rubber Division Meeting of the American Chemical Society in April:

1. "The Effect of Structural Modification on the Physical and Electronic Properties of Polythiophenes", J.P. Ruiz, J.R. Reynolds, K. Nayak and D.S. Marynick.

2. "Electrochemical Copolymerization as a Tool for the Study of the Mechanical and Electronic Properties of Polypyrrole", P.A. Poropatic, J.R. Reynolds, C.H. Huang and R.D. Goolsby.